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Adsorption Of Phosphorus From Wastewater Onto Biochar: Batch And Fixed-bed Column Studies

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Eutrophication has become a global environmental issue due to heavy agricultural activities. Phosphorus is one of the limiting nutrients governing the growth of algae and excessive release of phosphorus into aquatic environments has contributed significantly to the eutrophication process. Biochar, a low-cost adsorbent, has been proven to possess adsorption capacity, which can be utilized to remove pollutants from wastewater. This study was set out to investigate its ability to remove phosphorus in two different methods.

Biochar loaded with Fe^{3+} was prepared for batch experiments, in which an experimental design matrix had been created using factorial design methodology. The precursor of the biochar was wood biomass. Regression analysis was performed to create a model and study the individual effects and interaction effects of three independent variables, pH, initial concentration, and biochar dosage. The results showed that all variables had significant effect on the removal efficiency. Additionally, strong interaction effects were observed in two pairs, pH-Initial phosphorus concentration and pH-biochar dosage.

Natural biochar was used in fixed-bed column study to determine the impact of different flow rates on the removal efficiency, hydraulic loading rate, empty bed contact time, and saturation point. It was found that a higher flow rate led to a decrease of the removal efficiency. Moreover, the breakthrough point and saturation point occurred much faster.

Keywords	biochar, eutrophication, batch experiments, fix-bed column, phosphorus, phosphate, factorial design, regression analysis, ANOVA, pH, dosage

Contents

1 Introduction 1

2 Goal and Scope 2

3 Literature Review 3

3.1 Phosphorus 3
3.1.1 Phosphorus Cycle 3
3.1.2 Sources of Phosphorus 4
3.2 Eutrophication 5
3.2.1 Stages of the Eutrophication Process 5
3.2.2 Effects of Eutrophication 6
3.3 Phosphorus Treatment Technologies 8
3.4 Adsorption 10
3.4.1 Adsorption Mechanisms 10
3.4.2 Factors Affecting Adsorption of Phosphorus 11
3.5 Filtration 14
3.6 Fixed-bed Reactor 14
3.7 Biochar 16
3.7.1 Production of Biochar 16
3.7.2 Factors influencing Biochar Properties 17
3.7.3 Biochar Amendments 17
3.7.4 Biochar in Wastewater Treatment 18

4 Experimentation 19

4.1 Characteristics of Biochar 19
4.1.1 Bulk Density 19
4.1.2 Moisture Content 19
4.2 Biochar loading 19
4.3 Preparation of the Reagents 20
4.4 Experimental Design 20
4.4.1 DOE using 2^3 Factorial Design 20
4.4.2 Mathematical Modelling 22
4.5 Batch Experiments 23
4.6 Fixed-bed Adsorption Column Test 23
4.7 Analytical Method 25

5 Results and Analyses 25

5.1 Bulk Density and Moisture Content 25
5.2 Batch Experiments 26
5.2.1 Regression Analysis 26
5.2.2 Lack-of-fit Test 29
5.2.3 Non-linearity Test 30
5.2.4 Adjusted Determination of Coefficient 30
5.2.5 Two-way Interaction Effects 30
5.3 Fixed-bed Column 32

6 Discussion & Conclusions 34

6.1 Discussion 34
6.2 Conclusions 35
6.3 Limitations and Suggestions 36

References 37

Appendices
Appendix 1. Fixed-bed column experiment apparatus.
Appendix 2. R codes & summary statistics.

List of Figures

Figure 1. Pareto chart shows the ranking of the proportional effects of the parameters on the removal efficiency. 28
Figure 2. Two-way interaction between pH and initial TP concentration. 31
Figure 3. Two-way interaction between pH and biochar dose. 32
Figure 4. Breakthrough curve at different flow rates. 34

List of Tables

Table 1. Comparison of common treatment technologies for phosphorus removal. 9
Table 2. Main operating parameters for pyrolysis processes. 16
Table 3. Experiment levels and their corresponding physical values. 21
Table 4. Operating parameters of the column at V = 2.67 L/min. 24
Table 5. Operating parameters of the column at V = 4.01 L/min. 24
Table 6. Bulk density and moisture content of the biochar. 25
Table 7. Experimental design matrix and removal efficiency. 26
Table 8. Results of the first regression analysis for TP adsorption removal efficiency. 28
Table 9. Results of the second regression analysis, in which insignificant terms had been dropped. 29
Table 10. Parameters of the effluent at flow rate = 2.67 L/min. 33
Table 11. Parameters of the effluent at flow rate = 4.01 L/min. 33

Abbreviation

ANOVA : Analysis of Variance

CO_2 : Carbon Dioxide

DOE : Design of Experiment

EBCT : Empty-Bed Contact Time

EPBR : Enhanced Phosphorus Biological Removal

HCl : Hydrochloric Acid

HLR : Hydraulic Loading Rate

H_2S : Hydrogen Sulfide

H_2SO_4 : Sulfuric Acid

P : Phosphorus

N : Nitrogen

NaOH : Sodium Hydroxide

H_0 : Null Hypothesis

H_A : Alternative Hypothesis

HABs : Harmful Algal Blooms

TP : Total Phosphorus

DNA : Deoxyribonucleic Acid

RNA : Ribonucleic Acid

1 Introduction

As a universally accepted truth, water is the most essential element for all living species and there would be no life without it. Humanity has a long, interdependent and intricate relationship with water. The first civilizations were built in river valleys and other places where water was easily accessible because they offered many advantages in food production, commerce, transportation and recreational activities. However, water is a limited resource and only a small fraction of the total amount of water is usable for human beings. 72% of the Earth is covered in water, but saline water in the oceans takes up over 96 percent of that. Thus, the rest (about 3%) is freshwater, in which, approximately 99.7% is captured in icecaps and glaciers or stored in groundwater aquifers (Gleick, 1993). Surface water only amounts to about 0.3% of all the freshwater on Earth.

In the last few decades, rapid expansion of urban areas in terms of infrastructure and population has generated higher water demands, which tend to exceed the limits of carrying capacity of their regional water resources. Freshwater has become more vulnerable to contamination by sewage, industrial pollution and agricultural runoff as a result of significant increase of urban population. On the hydrological map of the world, eutrophication is one of the substantial threats causing deterioration of water ecosystems. Furthermore, climate change might considerably increase both the scale and the magnitude of the issues that we are facing. In many developing countries, water scarcity and water pollution happen frequently. Thus, economical and easy-to-perform treatment processes should be investigated and developed to tackle the issue. One approach to achieve that goal is to utilize wastes from different processes and sectors to treat wastewater.

Among numerous pollutants present in wastewater and water bodies, phosphorus is an impactful limiting element, which causes eutrophication in water bodies, ultimately leading to water degradation and demise of aquatic plants, animals together with other living microorganisms. Various treatment methods have been developed to treat water containing high concentrations of phosphorus. One of them is the use of carbonaceous materials to adsorb phosphorus from aqueous solutions. They can be used to polish water quality or to treat low strength wastewater for purposes other than drinking. Acti-

vated carbon is the most used adsorbent owing to its high surface area and porous structure. Although its adsorption capacity is high, the production cost of activated carbon is relatively expensive due to the high consumption of electricity for thermal activation and the addition of chemicals for chemical treatment.

Biochar is a porous carbonaceous material produced by thermochemical conversion of carbon-rich biomass in oxygen-limited condition (Shackley et al., 2012). In some respects, biochar is similar to activated carbon. However, biochar is not activated by thermal or chemical treatment, which makes the production more economical (Ahmad et al., 2012). The trade-off is that its surface area might be lower than that of activated carbon. Additionally, integration of biochar into soil improves the functionality of soil, making it more fertile (Van Zwieten et al., 2010). Numerous researches have demonstrated biochar's potential role in environmental management.

2 Goal and Scope

In this study, phosphorus removal from aqueous solutions was examined in batch experiments and by a fixed-bed column method using a low-cost biochar. A set of experiments conducted earlier showed poor removal efficiency (15%) using natural biochar at elevated temperature, 40 ^{o}C. Hence, it was decided that biochar loaded with Fe^{3+} would be used in batch experiments. Batch adsorption involves mixing the biochar, which had been pre-loaded with Fe^{3+}, with wastewater of different concentrations in beakers for 1 hour. Adsorption is a complex process, in which different variables such as pH, wastewater's initial phosphorus concentration, and adsorbent dosage might have varying effects on the removal efficiency for different adsorbents and pollutants. Hence, a 2^3 full factorial design was employed to create the experimental design matrix, and the effects of interactions between independent operating variables on the removal efficiency were examined to find the superior set of parameters within the study region. Finally, regression analysis was implemented to build a mathematical model, which describes the adsorption process in these specific batch experiments. In the packed-bed column study, the effect of flow rates on the removal efficiency of raw the biochar bed system after 1 hour was investigated. Additionally, a plot representing the initial part of a breakthrough curve was created to estimate exhaustion time of the bed at different flow rates. All the experiments and analyses were conducted at the Helsinki Metropolia University of Applied Sciences' environmental laboratory.

3 Literature Review

3.1 Phosphorus

Phosphorus is a macronutrient essential for the growth of plants and other biological organisms. This element is one of the fundamental building blocks that constitute nucleic acids (DNA and RNA), complex carbohydrates and phospholipids. In most cases of freshwater bodies, the limiting nutrient in regards to algal growth is likely to be phosphorus (Manahan, 2009). The common forms of phosphorus present in aqueous solutions are orthophosphate, polyphosphate and organic phosphate (Tchobanoglous et al., 2003). Generally, wastewater contains orthophosphate and small amounts of organic phosphate (Grubb, 2000). Industrial wastewaters from some industries might contain phosphate levels greater than 10 mg/L (Akay et al., 1998).

3.1.1 Phosphorus Cycle

The most significant difference of the phosphorus cycle compared to other element cycles is that no gaseous compounds exist. Therefore, it is only found in soil and aquatic environments. Since phosphorus is not readily available from the atmosphere, it is deemed the limiting nutrient. Overall, inorganic phosphorus is discharged into water bodies from numerous natural and human sources. When plants and animals die, decomposition of the biomass by bacterial activities converts organic phosphorus to inorganic phosphorus, which is then released back to the environment. The major steps of the phosphorus cycle in aquatic environments are summarized below (Bitton, 2010).

***Mineralization*:** Organic phosphorus compounds are mineralized to orthophosphate by microorganisms such as bacteria (e.g., Bacillus Subtilis), and fungi (e.g., Penicillium). The enzymes accountable for the decomposition of phosphorus compounds are phosphatases.

Assimilation: Microorganisms assimilate phosphorus into their cells.

***Precipitation of Phosphorus*:** In the aquatic environment, the solubility of orthophosphate is affected by the pH and the presence of other minerals, Al^{3+}, Ca^{2+}, Fe^{3+}, and

Mg^{2+}. Precipitation leads to formations of insoluble compounds, such as $Fe_3(PO_4)_2.8H_2O$ and $AlPO_4.2H_2O$.

***Solubilisation of Insoluble Phosphorus*:** Microorganisms' metabolic activity contributes to the solubilisation of phosphorus compounds. The process involves enzymes, production of organic and inorganic acids, production of CO_2, and production of H_2S.

3.1.2 Sources of Phosphorus

Since phosphorus is usually the limiting nutrient in lakes and rivers, in order to reverse or slow down the eutrophication process, the inputs of phosphorus to the water bodies must be abridged. This can be accomplished by identifying the sources of phosphorus and potential mitigation methods for their reduction. The natural source of phosphorus to lakes is from the weathering of rock and from decomposition of organic matter (Pery and Vanderklein, 1996). However, it is extremely difficult to regulate the natural inputs of phosphorus. As in the case of many lakes, the major sources of phosphorus are anthropogenic. These nutrient sources are categorized into non-point sources and point sources (Smith, 2003).

Point Sources

The most common sources of point discharges to water bodies are wastewater and industrial wastewater effluent, runoff and leachate from waste disposal sites, and runoff from animal feed lots. They tend to be continuous, with little variability over time. All municipal sewage contains phosphorus from human excrement and from detergents containing polyphosphate. Alexander & Stevens (1976) measured total phosphorus content in wastewaters in various countries and showed that the average concentration is about 1.4 g P/capital/day. Some industrial wastes also contain large quantities of this nutrient (Davis and Cornwell, 2007). Over the last decades, there has been a significant reduction of number of point inputs of water pollution, because of their relative ease of identification and control (Carpenter et al., 1998).

Non-point Sources

In contrast to point sources, non-point discharges are difficult to measure and control. Most of the time, they are discrete and linked to seasonal agricultural activities or irreg-

ular events, such as land fertilization, heavy precipitation, or septic leakage. Due to their long-range transport ability, phosphorus is conveyed overland or underground to receiving waters. Among these sources, agricultural runoff contributes the most to eutrophication. Phosphorus not taken up by plants is bound to soil particles, and is carried to lakes through soil erosion. Excessive application of fertilizers and inadequate management practices enhance nutrient leaching into waters (Khan and Ansari, 2005). In addition, rainwater also carries some of the phosphorus to water bodies (Carpenter et al., 1998).

3.2 Eutrophication

Eutrophication is characterized by the excessive production of algae and plants in an ecosystem, as a result of an enhanced enrichment of nutrients (Schindler, 2006). Limiting nutrients are found to be nitrogen and phosphorus in most cases and the general order of deficiency is P > N (Forsberg, 1976). Naturally, eutrophication occurs in water bodies over a long period of time as they age and are filled with sediments (Carpenter, 1981). However, increase in the intensity of agricultural and industrial activities, due to the explosion of human population, has accelerated the rate and extent of eutrophication. Increasing economic growth also indirectly contributes to the issue since it leads to changes in diets and agricultural extension to accommodate the demand. Once a lake has become eutrophic, it could take 1,000 years or more to remediate (Carpenter, 2005).

3.2.1 Stages of the Eutrophication Process

As with any ecological process, eutrophication is dynamic and is an indication of the functions and structures of aquatic biological communities, of their adaptation to new changes arising in the water environment. Four main stages are described briefly below (Browne, 2011).

The process is triggered by the increase of excessive nutrients level above regular values in the ecosystem.

In the second stage, an escalation of biological productivity leads to the production and overgrowth of aquatic plants and algae. A thick layer of floating algae is formed.

The third phase corresponds to the death and decomposition of algae and aquatic plants at the bottom of the water body. During this phase, the oxygen content is depleted and eventually, is used up as decomposition of biomass accelerates. Anaerobic conditions appear in the water, which leads to denitrification, followed by sulphate reduction. Hydrogen sulfide (H_2S) is formed as waste by sulfate-reducing bacteria.

The fourth stage is manifested by the continuous supply of water with nutrients and further degradation of water quality. The release of H_2S and ammonia contributes to the process because nutrients are prevented from settling down. Several chemical reactions brought about by anoxic conditions in waters are as follows (CH_2O signifies decomposing organic matter):

Aerobic respiration: $CH_2O + O_2 \rightarrow CO_2 + H_2O$
Denitrification by bacteria: $5CH_2O + 4NO_3 \rightarrow 2N_2 + 4HCO_3^- + CO_2 + 3H_2O$
Sulphate reduction: $2CH_2O + SO_4^{2-} + H^+ \rightarrow H_2S + 2HCO_3^-$
Methane formation: $2CH_2O \rightarrow CO_2 + CH_4$
Iron reduction: $CH_2O + 7CO_2 + 4Fe(OH)_3 \rightarrow 4Fe^{2+} + 8HCO_3^- + 3H_2O$

3.2.2 Effects of Eutrophication

Eutrophication has become a global environmental issue; within a few decades, many aquatic bodies have transformed to eutrophic condition. The effect of eutrophication is not limited only to the ecological characteristics of the water bodies, but can also cause severe social-economic damages.

Impacts on the Ecosystem

Various aspects of the ecosystem can be negatively impacted by eutrophication. The intensive algal growth causes replacement of corals with filamentous algae, macroalgae, and numerous filter feeders (Foden et al., 2011). Bottom-water hypoxia led to diminished aquatic vegetation and aquatic species. High production of CO_2 accompanied by high organic decomposition rate enhances water acidification.

Eutrophication is also an ecological threat to benthic life in many coastal areas, mainly because of the resulting hypoxia and anoxia conditions occur during the third stage as described above. Rosenberg et al. (2002) reported a total loss of benthic macrofauna biomass of 3 million tonnes in some parts of the Baltic Sea due to increased nutrient enrichment. Rybicki et al. (1997) observed loss of submersed macrophyte beds due to the increase of suspended particles, which are trapped on the seabed. Accelerated eutrophication negatively impacts important habitats (e.g., sea grass and shellfish bed) together with fish nursery areas. Accumulation of hydrogen sulfide intensifies stress on the ecosystem, creating toxic inhabitable environments under water, resulting in mass death of submerged aquatic vegetation, aquatic animals and macrozoobenthos.

Effects on Phytoplankton Community

Besides proliferating extensive phytoplankton blooms in all aquatic habitats, excessive addition of nutrients (P and N) also cause change in the specification of phytoplankton. Some phytoplankton species have changed to larger forms of diatoms (Furnas et al., 2005). Changes in phytoplankton communities in eutrophic waters result in significant fluctuations at other areas. The growth of certain types of phytoplankton, which are beneficial for mussels and other aquatic species, is impeded (Starr et al., 1990).

Harmful Algal Blooms (HABs)

HABs are one of the growing frequent threats to aquatic ecosystems worldwide (Glibert et al., 2005). They can cause damaging effects to both aquatic animals in localized areas and the whole ecosystem by activities such as poisoning by toxins (Kim et al., 2002; Brand et al., 2011) and clogging of fish gills (Graneli and Turner, 2008). While the effects of increasing eutrophication on HABs are complicated, recent researches suggest the process is likely to enhance the frequency and magnitude of these events (O'Neil et al., 2011).

Cyanobacteria, which blooms as the most harmful algae can cause many nuisance or impairment to the environment, such as thick scum mats on the surface water (Van Rijin and Shilo, 1985), production of hepatotoxins and neurotoxins (Namikoshi and Rinehart, 1996), and human death (Chorus and Bartram, 1999). In addition, booms of phytoplankton and macroalgae circumscribe light penetration, causing low water clarity and hindering photosynthetic processes of benthic plants and sea grasses in littoral

zones. The HABs also indirectly affect marine animals because they pose threats to the health and reproduction of invertebrates, which are the most essential nutrient sources of many oceanic animals. In the Gulf of Finland, cyanobacteria blooms were the source momentous reduction in copepod egg production (Sellner et al., 1996).

Socio-economic Effects

The recreational value of eutrophic waters is reduced because of the unpleasant odour and view. Excessive plant growth might hinder marine navigation. If the water is intended for potable use, the costs of treatment are increased. Algal biomass may clog filters in treatment plants; thus, they have to be cleaned more frequently. Many algae release neurotoxins, which have detrimental effects on fish, mussel, and other livestock. As a result, the fishery industry is damaged, leading to job insecurity (Lester and Birkett, 1999).

3.3 Phosphorus Treatment Technologies

In the field of wastewater treatment technology, numerous techniques have been implemented to remove phosphate. They fall into three main categories: biological, chemical, and physical. Physical methods such as reverse osmosis and electro dialysis are too expensive, whereas others are ineffective, reaching only 10% removal efficiency (Yeoman et al., 1988). Enhanced biological treatment method can achieve 97% removal of total phosphorus, but operational difficulties make it unstable (Onar et al., 1996). Chemical techniques are the most effective and well-studied methods, including phosphate precipitation with different salts such as calcium and aluminium (Yeoman et al., 1988). However, the use of salts increases the costs, and the amount of sludge generated; therefore, this method has not been applied widely (Clark et al. 1997). Besides, phosphorus precipitation by metal salts makes the precipitate unrecoverable for potential processing into fertilizer (Donner and Salecker, 1999; De-Bashan and Bashan, 2004).

Another chemical technique, adsorption, has proven to be economical because the only cost associated with the adsorbents is transportation (Boyer et al., 2011). Moreover, there is no sludge generated from the process. Low-cost and readily available materials or agricultural by-products have been extensively investigated for some decades. Activated carbon derived from various wastes is effective in the removal of phos-

phorus. Nonetheless, the process requires high amount of energy as well as the application of chemicals for activation. Many researches have been conducted to find raw materials, which can be used as they are or with little modification, for phosphorus removal. Can and Yildiz (2005) reported a removal efficiency of 99,6%, corresponding to the operating conditions of 25 mg/L initial phosphate concentration, 2 g/L fly ash dosage and 5,5 pH level. Phosphate removal of 99% using gas concrete, a building material, was shown in a study by Oguz et al. (2003). Table 3 demonstrates comparison of different treatment technologies for phosphorus removal.

Table 1. Comparison of common treatment technologies for phosphorus removal.

Process	**Advantages**	**Disadvantages**	**Eff. Quality**	**References**
Chemical precipitation	Flexible/Easy operation; effective; less space is required.	Sludge production (significantly high if lime is added); P cannot be recycled; chemicals addition.	0.005-0.04 mg P/L	Strom (2006) Tchobanoglous et al. (2003) Morse et al. (1998)
EPBR	High P removal at modest cost; minimal sludge production	Energy consumption; more space is required; cold climate might be a challenge; more complicated configurations.	0.02 – 0.1 mg P/L	Morse et al. (1998) Strom (2006) Tchobanoglous et al. (2003) Mino et al., (1998)
Crystallization	Final product can be used as fertilizer.	Increased salinity; complex process.	0.3-1 mg P/L	De-Bashan and Bashan (2004)
Constructed Wetlands	No additional sludge; low installation and maintenance cost; habitat for some animals.	Susceptibility to climate; accumulation of heavy metals and hazardous pollutants.	Poor	De-Bashan and Bashan (2004)

3.4 Adsorption

Adsorption is the accumulation or enrichment of chemical substances onto a surface or interface. The adsorbing phase is defined as the adsorbent, and the material being adsorbed the adsorbate. The adsorbent is required to have an extremely large surface area on which the adhesion of contaminants can occur. It can occur between two phases, such as: gas-liquid, gas-solid, liquid-liquid, or liquid-solid interface. In the field of water treatment, adsorption has been proven as an efficient removal process for numerous types of pollutants, where ions or molecules are removed from liquids by adsorption onto solid surfaces (Worch, 2012).

Solid surfaces are active and energetic sites, which are able to interact with solutes due to their specific electronic and spatial properties. Since adsorption is a surface-based process, the surface area plays an important role in determining adsorbents' quality (Crittenden, Crittenden and Thomas, 1998).

3.4.1 Adsorption Mechanisms

Four main steps of the process can be summarized as follows (Soleto et al., 2013):

a) Solute is transferred from the liquid to adsorbent's boundary layer.
b) External diffusion occurs, whereby the solute is transferred to the surface of the adsorbent through the boundary layer.
c) The solute is diffused from the surface to active sites, termed intra-particle diffusion.
d) Sorption of the adsorbate to the solid phase, by several forces described below.

In most cases, two primary driving forces lead to the adsorption of a solute from an aqueous. The first driving force is linked with the solvent disliking (lyphobic) character of the solute. A hydrophobic substance tends to be adsorbed while a hydrophilic substance tends to stay in the water. The solubility of a dissolved substance is essential in determining the intensity of adsorption process. The second driving force is the electrical attraction of the solute to the solid. This type occurs as a result of chemical interaction or van der Waals attraction with the adsorbent. The adsorption induced by van der Waals force is defined as physisorption, and the other type of adsorption is termed as

chemisorption. In adsorption processes, these two types interact together and it is quite difficult to differentiate between the two (Cecen and Aktas, 2012; Worch, 2012).

Chemisorption

In chemisorption, electrons in specific surface sites and solute molecules are exchanged, resulting in the formation of a strong chemical bond. Chemically adsorbed adsorbates are immobilized within the surface or on the surface. Since chemical reactions happen more rapidly at higher temperatures, chemisorption is more predominant at high temperatures compared to physical adsorption. It also has high adsorption enthalpy (40-800 kJ/mol) (Cecen and Aktas, 2012).

Physisorption

In physisorption, intermolecular attractions occur between favourable energy sites. The adsorbate is attached to the surface by weak van der Waals forces in physisorption, hence it is less strongly attached to the surface compared to chemisorption. There is not any exchange of electrons in this process. In contrary to chemisorption, physical adsorption is predominant at temperatures below 150 ^{o}C and its adsorption enthalpy is low (5-40 kJ/mol) (Cecen and Aktas, 2012).

3.4.2 Factors Affecting Adsorption of Phosphorus

Adsorption is not a homogeneous process and a variety of factors affect its efficiency. Besides physical properties of the adsorbent such as porosity, internal surface area, and external surface area, wastewater's properties also have significant influences on the overall removal efficiency. The most important characteristics of the feed solution and the adsorbents are reviewed below.

pH

The effect of pH on the bio-sorption of phosphorus onto different adsorbents has been investigated in many studies. Coir-pith carbon activated chemically by H_2SO_4 achieved the highest adsorption of phosphorus in the pH range of 6-10 (Kumar et al., 2010). In another study, Benyoucef and Amrani (2011) reported the effective pH range for phosphate uptake by Aleppo pine sawdust to be 3.5-7.5. Krishnan and Haridas (2008) ob-

served that phosphorous was effectively removed from wastewater by natural coir pith in the pH range of 2.0 - 3.5. Xu et al. (2011) explored that modified cotton stalk removed phosphorus efficiently in the pH range of 4 - 9. Varying results on the influence of pH on the adsorption process indicate its complex nature. However, most results infer that the optimum pH is slightly acidic to around neutral (4 - 7) for the majority of sorbents.

Temperature

Adsorption is affected by the relations between the properties of the adsorbent and the solute. Thus, the effects of temperature are different for different adsorbents and solutes. In general, numerous studies have shown that by increasing the temperature of the solution to a specific range, the adsorption efficiency of different adsorbents also increases. Saha et al. (2010) found that at pH 3, the maximum amount of phosphate adsorbed per gram of added granular ferric hydroxide occurred at 45 ^{o}C. Mezenner and Bensmaili (2009) showed that the phosphorus adsorption capacity of iron hydroxide eggshell increased as the solution was heated from 20 to 45 ^{o}C. Benyoucef and Amrani (2011) attributed the higher phosphorus adsorption capability with increasing temperature to the expansion of pore size at higher temperatures. Moreover, Kumar et al. (2010) suggested that elevated temperature leads to an increase in the rate of diffusion of phosphate ions, which in turn enhances the adsorption efficiency. However, it is important to note that higher temperature is not always beneficial for the process. In a study conducted by Yue et al. (2010), there was a decrease in the phosphorous sorption capacity of modified giant reed as the temperature increased from 30 ^{o}C to 60 ^{o}C. The researchers proposed that desorption of phosphate ions from the adsorbent surface might be accelerated at this temperature range.

Adsorbent Dosage

All scientific studies indicated that phosphorus adsorption increased with increasing adsorbent dose up to a specific level, and then it remained constant. One simple explanation for this is that by adding more adsorbent to the solution, more binding sites are available for the sorption process. Thus, high amounts of phosphate ions can be adsorbed. In most studies, the range of adsorbent dosage is between 0.5 and 2 g/L for 250 mL wastewater (Kumar et al., 2010).

Contact Time

The design and economics of any adsorption system are heavily influenced by the process' kinetics. The required contact time varies between different adsorbents and contaminants. Generally, the adsorption of phosphorus by most adsorbents reached equilibrium in less than 1 hour. The adsorption of phosphorus by modified giant reed reached equilibrium after 25 minutes (Yue et al., 2010). Xu et al. (2009) reported the adsorption of phosphorus on modified wheat residue reached equilibrium after 10 minutes, whereas 30 min was required in the case of using hydroxide-eggshell (Mezenner & Bensmaili, 2009). Benyoucef and Amrani (2011) observed the process reached equilibrium after 40 minutes when using modified Aleppo pine. Contrariwise, several studies reported slower uptake speed. 3 h was necessary for the removal process by coir pith activated carbon to reach equilibrium (Kumar et al., 2010). In another study by Biswas et al. (2007), the phosphorus uptake by metal-loaded orange waste only reached equilibrium after 15 hours. Some authors have concluded that processes occurring in less than one hour are more favourable and get more ready acceptance in the science community than those requiring longer contact time (Wase and Forster, 1997).

Initial Concentration

Generally, the adsorption efficiency decreases if there is a significant increase in the initial concentration of phosphate. The percentage adsorption of phosphate onto iron hydroxide eggshell decreased from 95% to 64% when initial phosphate concentrate increased from 2.8 mg/L to 110 mg/L (Mezenner and Bensmaili, 2009). However, in another study by Xu et al. (2009), they observed an increase in phosphate uptake capacity when the initial concentration was raised from 100 mg/L to 300 mg/L.

Interfering ions

Since wastewater contains various anions, which may interfere in the process, many researchers have studied their potential effects on the adsorption efficiency. Divya et al. (2012) stated that the presence of anions like Cl_2, SO_4^{2-}, NO_3^- and CO_3^{2-} did not show any significant influence on phosphate adsorption, whilst some cations such as Ca^{2+}, Mg^{2+}, Cu^{2+}, Fe^{2+} and Zn^{2+} facilitate the process. These findings coincide with those reported by Chen et al. (2014). They concluded that anions of Cl^-, NO_3^-, and

SO_4^{2-} had a negligible effect on phosphorus adsorption by natural pyrite. On the other hand, a study conducted by Zhang et al. (2012) showed that SO_4^{2-} and CO_3^{2-} had a negative influence on the phosphate uptake of lanthanum-doped activated carbon fibre. These results demonstrated the complex nature of adsorption process, especially when competing ions are involved.

3.5 Filtration

Filtration is the mechanical or physical process of removing impurities (e.g. suspended solids, coagulated particles etc.) from wastewaters by passing the liquids through a porous material, called a filter. Regularly, the filter media can be sand, cloth, anthracite, activated carbon, garnet sand, or a combination of these materials. The filtrate refers to the liquid passed through the filter. Filtration process is primarily dependent on a combination of complicated chemical and physical mechanisms, with adsorption being the most essential one (Pizzi, 2010).

There are two main types of filter, gravity filter and pressure filter, with the former one being more commonly used. For pressure filters, addition pressure is applied to the water, forcing it through the filter. Meanwhile, for gravity filters, the gravitational force conveys the water through the filter.

3.6 Fixed-bed Reactor

Fixed-bed reactor is a process that combines adsorption and filtration to remove wastewater containing little or no suspended solids. Two main classes are up-flow and down-flow reactors, in which wastewater flows through the adsorbent bed, and is discharged either at the top or the bottom of the column (Cecen and Aktas, 2012). The working principle of fixed-bed adsorption is similar to that of granular filtration. Van der Waals forces affect both adsorption and particle deposition. It should be noted that adsorption columns with diameters greater than 2 cm could regularly be scaled-up linearly (Sibrell and Tucker, 2012).

During the operation of the system, several principal factors affecting the removal efficiency and the stability, which must be taken into account, are the hydraulic loading rate, the bed depth, the empty-bed contact time (EBCT), and the saturation time.

Hydraulic Loading Rate (HLR)

The hydraulic loading rate is the total flow of wastewater applied on unit area of the adsorbent bed over a specified time period, and it can be expressed as:

$$HLR = \frac{Q}{A} \quad \text{(Eq. 1)}$$

where *HLR* is the hydraulic loading rate (m^3/m^2s), *Q* is the flow rate (m^3/s), and *A* is the cross-sectional area of bed (m^2).

Empty-Bed Contact Time (EBCT)

The EBCT is used to measure the contact between an adsorbent, such as biochar, and wastewater as it flows through a bed packed with the material (Gupta and Suhas, 2009). As the EBCT increases, the time available for adsorption process also increases. Eq. (2) can be used to calculate the parameter.

$$EBCT = \frac{V_{bed}}{Q} = \frac{Z}{U} \quad \text{(Eq. 2)}$$

where *EBCT* is the empty-bed contact time (min), V_{bed} is the adsorbent bed volume (cm^3), *Q* is the flow rate (m^3/s), *Z* is the bed depth of the column (cm), and *U* is the linear flow rate (cm/min).

Saturation Time

The saturation point is reached when the effluent concentration becomes equal to the initial concentration, i.e. the pollutant is not adsorbed anymore. The time at which breakthrough appears is an important property for determining the operation of a fixed-bed column. It is expressed in terms of normalized concentration, defined as the ratio of outlet concentration to inlet concentration (C_t/C_i) as a function of time for a given bed height (Kundu et al., 2004). High flow rates generally cause the breakthrough and saturation time to occur faster because the contact time is decreased, which hampers the phosphate diffusion into adsorbents' pores. Although adsorption is a relatively fast process, diffusion requires longer residence time of wastewater in the column. As a result, low flow rates are generally favourable for effective removal of contaminants in fixed-bed column mode (Song et al., 2011; Ahmad and Hameed, 2010).

3.7 Biochar

Biochar is a porous carbonaceous residue produced by pyrolysis of carbon-rich biomass under low temperatures (< 700 ^{o}C) and oxygen-limited condition (Lehmann and Joseph, 2009). Normally, agricultural residues are the precursors due to their availability in large amounts and inexpensive prices. A life cycle impact assessment of different biochar production methods, conducted by Roberts et al., in 2010, has proven this point. Several papers have indicated that it can be used as soil amendments to improve soil nutrient-holding capacity (Novak et al. 2009) and benefit favourable living microorganisms (Kolb et al. 2009). It is also suggested that it can mitigate global warming by reducing emissions of carbon dioxide and other greenhouse gases from soils (Verheijen et al., 2010). Additionally, biochar has been shown to remove different types of pesticides and other hazardous environmental pollutants (Chen and Chen, 2009).

3.7.1 Production of Biochar

Pyrolysis is described as the thermochemical degradation of raw, dried lignocellulosic materials in the absence of oxygen/air at elevated temperatures to produce carbonaceous char, oil and combustible gases. (Sanghi and Singh, 2012). Depending on the operating conditions, the pyrolysis process can be divided into three regimes: slow pyrolysis, fast pyrolysis, and flash pyrolysis. Slower rates of heating increase the production of char, whereas faster heating rates result in higher yield of liquid product. Table 2 shows main operating parameters for different pyrolysis processes (Demirbas and Arin, 2002).

In general, a low temperature and low heating rate condition, as in the case of slow pyrolysis, is ideal for a high biochar yield. On the contrary, if the purpose is to maximize the yield of bio-oils, a high heating rate, short residence time, and high temperature would be preferred (Demirbas, 2006). Another important factor influencing the properties of biochar is the quality of the biomass.

Table 2. Main operating parameters for pyrolysis processes.

	Slow Pyrolysis	**Fast Pyrolysis**	**Flash Pyrolysis**
Temperature (^{o}C)	130-680	580-980	780-1030
Heating rate (^{o}C/s)	0.1-1	10-200	> 700

Particle size (mm)	5-50	< 1	< 0.2
Residence time (s)	450-550	0.5-10	< 0.5
Products	35% biochar, 35% gas, 30% liquid	12% biochar, 13% gas, 75% liquid	80% liquid, 20% biochar + gas

[Adopted from (Demirbas and Arin, 2002) and (Bolan et al., 2013)]

3.7.2 Factors influencing Biochar Properties

Typically, biochar yield is reliant on the feedstock type (poultry litter, wood biomasses, and crop residues) and the conditions during pyrolysis. Enders et al. 2012 showed that chicken litter generated a higher yield than that from wood biomasses. It might be due to the presence of various metals in animal litter, which protects against the loss of volatile material (Cantrell et al., 2012). On the other hand, biochar produced from poultry litter and solid wastes exhibit lower surface areas compared to biochar generated from pyrolysis of wood biomasses (Bourke et al., 2007). Among all process parameters, pyrolysis temperature is the most important one. In one study, carbon content of biochar increased from 56% to 93% when temperature increased from 300 ^{o}C to 800 ^{o}C (Okimori et al., 2003, cited in Sohi et al., 2010). In another research, Ahmad et al. (2012) concluded that high pyrolysis temperature (at 700 ^{o}C) resulted in amplified surface area of biochar derived from soybean stover and peanut shell. Uchimiya et al. (2011) also found that biochar yield decreased at ≤ 400 ^{o}C after testing biochar generation from cottonseed hulls at different temperatures, ranging from 200 ^{o}C to 800 ^{o}C. As indicated in a study conducted by Angin (2012), heating rate is the least significant factor in determining biochar yield.

3.7.3 Biochar Amendments

Biochar has the potential to improve physiochemical and biological properties of soil thanks to its high organic C content. Substantial increases in plant growth and crop yields have been observed in studies of biochar addition to soil (Glaser et al., 2002). Moreover, crop yields can be improved significantly if biochar is applied together with inorganic or organic fertilizers (Glaser et al., 2002). Verheijen et al. (2010) reported an increase of both microbial activity and microbial population in soil ameliorated with biochar. These changes affect biogeochemical processes in soil. On the other hand, additions of large amounts of biochar may also have negative impacts on some pH-

sensitive plants. An addition of 5 Mg biochar per hectare resulted in a decrease of soybean yield (Kishimoto and Sugiura, 1985, cited by Glaser et al., 2002). However, in general, crop yields did not drop after the application of biochar.

Integrating biochar into the soil structure can enhance not only the nutrient contents but also the water and nutrient retention. Its high surface area combined with improved soil structure boost water-holding capacity of soil. As shown in a study conducted by Tryon (1948), soil water retention capacity increased by about 18% upon addition of 45% (by volume) biochar to a sandy soil. Laird et al., (2010) also reported a reduction of nutrient leaching from Mid-western agricultural soil due to biochar application. Lehmann et al. (2003) observed that amendment of biochar considerably reduced the leaching of N. This helps to mitigate eutrophication indirectly since the amounts of nutrients effused into water bodies are reduced.

In spite of the potential benefits of biochar applications, the interactions between biochar and soil have not been completely understood in all cases. Hence, it is advisable to monitor long-term effects of biochar applications on different types of soils.

3.7.4 Biochar in Wastewater Treatment

Sorption of contaminants from wastewater onto biochar occurs due to its high surface area and porosity (Lou et al., 2011). While most of the studies on biochar application are focused on soil amendment, there has been a growing interest in using biochar to treat wastewater. Some studies have shown that biochar can be an effective adsorbent for sorption of heavy metals from wastewater (Chen et al., 2011; Cao et al., 2009). However, only a few researchers have investigated the possibility of using biochar to remove phosphate from wastewater. Not only biochar embodies a low-cost technology, but the used biochar can also be marketed as a fertilizer to enhance soil fertility.

4 Experimentation

4.1 Characteristics of Biochar

4.1.1 Bulk Density

The bulk density, ρ_b, is an important parameter for determining the mass/volume ratio of adsorbers. It is calculated as the ratio of the adsorbent mass (m_A) and the total volume (V_A), which includes the adsorbent volume and the volume that fills the space between the particles:

$$\rho_b = \frac{m_A}{V_A} \quad \text{(Eq. 3)}$$

In this thesis, measurement of the bulk density of the oven-dried biochar was carried out by filling a known mass of the adsorbent in a graduated cylinder. The occupied volume was then recorded for calculation, according to Eq. (3). The measurement was repeated 3 more times to take the average value of the parameter. Additionally, the standard deviation was calculated to quantify the amount of variation in the results.

4.1.2 Moisture Content

In order to determine the moisture content of the biochar, 5 crucibles were filled with relatively equal amount of biochar (approximately 15 mg each), then the total mass of each crucible containing added biochar was determined. Afterwards, all the crucibles were placed into an oven and dried for 24 hours at 120 ^{o}C. The new weight of each crucible was measured, and the results are reported in Table 6.

4.2 Biochar loading

The biochar was manually crushed to desired sizes. A solution containing 100 mg/L of ferric sulfate was prepared and mixed with the biochar in a beaker for 2 hours. Subsequently, the mixture was poured into a crucible and placed in an oven pre-set to 100 ^{o}C for 12 hours. The biochar loaded with Fe^{3+} was used for the batch experiments.

4.3 Preparation of the Reagents

A wastewater sample solution obtained from a chemical company with initial TP concentration of 1800 mg/L was diluted to 18 mg/L for the column tests, and 20 mg/L, 30 mg/L and 40 mg/L for the batch experiments. The sample's composition is included in Appendix 1. The pH was adjusted by adding either HCl or NaOH to the solution prior to each experiment. The influence of HCl or NaOH on ionic strength could be neglected (< 1%) (Chen et al., 2010).

4.4 Experimental Design

4.4.1 DOE using 2^3 Factorial Design

In this thesis, experimental design was utilized to avoid having to conduct time-consuming and less explanatory one-factor-at-a-time experiments. Interactions arise when the effect of one process parameter on the response is dependent on the level of the other parameter. Interaction between variables is a common phenomenon and this methodology systematically tackles that by changing all variables from one experiment to the next, forming all possible combinations (Box et al., 2005). Four replicates of the centre point were conducted to determine the repeatability and the experimental error of the experiments. It also provides required information for testing lack-of-fit and non-linearity while not involving a large number of design points (Myers et al., 2009). The set of trials was randomized to minimize the effect of disturbances or uncontrollable external factors.

Three independent factors, namely pH (X_1), initial concentration of TP (X_2), and biochar dosage (X_3) were studied at two levels, high and low, coded as (+1) and (-1), respectively. The centre point's real parameters were designated as (0). Physical parameters were coded according to Eq. (6). Other experimental factors such as contact time, temperature, and speed of agitation were kept constant. For this thesis, a total of 12 experiments were required, including 4 replications of the centre point, as calculated from the following equation:

$$N = 2^k + n_c = 2^3 + 4 = 12 \qquad \text{(Eq. 4)}$$

where *N* is the total number of experiments, *k* is the number of factors and n_c is the number of centre point replicates.

The range of the variables for the experiments was mostly based on earlier studies, as discussed earlier. Two pH parameters, 4 and 7 for the low and high level, respectively, were chosen because, within this range, the dominant phosphate ions were $H_2PO_4^-$ and HPO_4^{2-}, which have strong affinity for adsorption sites (Yue et al., 2010). At higher pH, the repulsion force between the negatively charged surface sites and these negative charged ions might occur. Since the biochar was not activated, the adsorption capacity is expected to be lower than that of treated adsorbents. Hence, the dosage of biochar is higher in this study. The wastewater-to-biochar ratio is 1.5:100 and 2.5:100 at the low (-1) and high (+1) level, respectively. In previous researches, the ratio was lower, for instance, 1.5:250 or 2.0:250 at low level.

The relationship between the coded and physical form of the variables is as follows:

$$Coded\ Value = Z = \frac{X_i - \overline{X_i}}{\Delta X} \quad \text{(Eq. 5)}$$

Where X_i is the actual value of the factor in physical unit, $\overline{X_i}$ is the average of the low and high level, and ΔX denotes the step change. The coded values of the variables as well as their corresponding physical values are listed in the following table:

Table 3. Experiment levels and their corresponding physical values.

Variables	**Levels**		
	- 1	0	+1
pH	4	5.5	7
Initial C. mg/L	20	30	40
Dosage g/L	1.5	2	2.5

The response is removal efficiency in percentage, which can be calculated according to Eq. 6:

$$RE = \frac{C_i - C_f}{C_i} \times 100 \quad \text{(Eq. 6)}$$

where *RE* is the removal efficiency (%), C_i and C_f are the initial and equilibrium TP concentrations in the solution (mg/L).

The experimental data in an adsorption study can also be expressed in terms of an uptake of phosphorus, *Q*, defined as the amount of phosphorus adsorbed per unit mass of the adsorbent (mg/g), and evaluated using the following equation:

$$Q = C_i - \frac{C_f V}{m} \quad \text{(Eq. 7)}$$

where C_i and C_f are the initial and equilibrium P concentrations in the solution (mg/L), respectively, *V* is the solution volume (L), and *m* is the mass of adsorbent (g).

4.4.2 Mathematical Modelling

Regression analysis is a modelling technique for analysing the connection between a dependent variable (response) and independent variables. A linear plus pair-wise interaction equation was developed to predict the single response, removal efficiency, as a function of mentioned model terms. The model fitted to the 2^3 factorial design data including linear and interaction terms can be expressed as:

$$Y_i = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{123} X_1 X_2 X_3 \quad \text{(Eq. 8)}$$

where Y_i is the predicted response, β_0 is the intercept coefficient, $\beta_1 - \beta_3$ are the linear terms; $\beta_{12}, \beta_{13}, \beta_{23}, and\ \beta_{123}$ are the interaction terms; and X_1, X_2, and X_3 represent the coded independent variables. The coefficients of the model were estimated using ordinary multiple linear regression technique.

After fitting the model, several statistical analyses were conducted to determine the experimental error, the significance of the terms in the model, and the goodness of fit of the model. In cases where some model terms turn out to be statistically insignificant, the terms were dropped to make a subset of the model with only significant terms. The final model was then tested for non-linearity, lack-of-fit and comparability between the adjusted R-squared and the Q-squared was checked. The Q-squared coefficient is used to assess the predictive validity associated with the R-squared using leave-one-out validation. This model was then used to create graphical representations of various phenomena such as parameter dependencies and interactions between the parameters (Wächter and Cordery, 1999).

4.5 Batch Experiments

In order to study phosphate removal efficiency and effects of different variables on the process, batch experiments were conducted according to experimental design matrix given in table ab.cd. In each experiment, 100 ml of the phosphate solution was poured into 250 ml glass beaker and its pH was adjusted dropwise with either 0.1M HCl or 0.1M NaOH. A Mettler Toledo SevenGo Meter, previously calibrated with 4.0, 7.0, and 10.0 pH buffer solutions, was used to determine the pH. A known amount of biochar loaded with Fe^{3+} was then added to the solution and mixed by magnetic stirrer at 250 rpm for 1 hour. Finally, the adsorbent was separated from the solution by filter paper, and the remaining aqueous solution was pipetted into a LCK 348 cuvette for analysis.

4.6 Fixed-bed Adsorption Column Test

The continuous flow fixed-bed experiment was performed to determine the change in phosphorus removal efficiency after 1 hour of operation at two different flow rates. The wastewater's temperature remained the same, at 27 ± 1°C. The apparatus included a plastic column of 10 cm internal diameter and 170 cm length), a Wilden air-operated diaphragm pump, and a wastewater tank. Biochar was packed into the column between two layers of plastic pellets, which help to fix biochar position. The depths of the layers were 70 cm pellet, 50 cm biochar, and 70 cm pellet in all trials. Prior to the experiments, fines were removed from the column by passing distilled water through the materials (Droste, 1996).

In order to avoid channelling and ensure a uniform streaming, up-flow mode was chosen. The particle sizes of 0.5 - 1 cm were used so that the column-to-particle diameter is ≥ 10. This helps to reduce the effect of pressure drop and avoid handling issues (Worch, 2012). The particles are still small enough to provide reasonably more surface area for the process and less resistance to mass transfer, resulting in a more effective uptake of phosphorus. A solution containing 18 mg P/L in tap water was fed to the column, and pumped through the bed at constant linear velocities of u_1 = 34 cm/min and u_2 = 41 cm/min. The corresponding flow-rates through the tube were approximately 2.67 L/min and 4.01 L/min. In terms of bed volume of the effective bed, about 41 bed volumes had been passed through the column after the first test, and 61 bed volumes

had been passed through the column after the second one. A small hose connected to a valve was installed to the top of the column to collect samples for analysis. In total, 4 samples were collected for TP concentration analysis at regular time intervals. The pH of the influent was 5.5 and the effluent's pH was recorded afterwards. Operating parameters of two experiments are summarized in Table 4 and Table 5.

The total amount of TP flowed through the column was calculated from Eq. (9).

$$M_{total} = \frac{C_i V t}{1000} \quad \text{(Eq. 9)}$$

where M is the total mass of TP (mg), C_i is the inlet concentration (mg/L), V is the volumetric flow rate (L/min) and t is the operating time (min).

The ratio between initial TP concentration and TP concentration at different time t was calculated from Eq. (10), which was then used to construct the breakthrough plot.

$$Normalized\ concentration\ (ratio) = \frac{Ct}{Ci} \quad \text{(Eq. 10)}$$

where C_i is the initial TP concentration and C_t is the TP concentration in the effluent at time t.

Table 4. Operating parameters of the column at V = 2.67 L/min.

Column Volume cm^3	13352	**HLR cm^3/cm^2s**	0.57
Cross-sectional Area cm^2	78.54	**EBCT min**	1.471
Biochar Bed Volume cm^3	3927	**M_{60} mg**	2900
Flow cm^3/min	2670.35	**Linear Velocity cm/min**	34

Table 5. Operating parameters of the column at V = 4.01 L/min.

Column Volume cm^3	13352	**HLR cm^3/cm^2s**	0.85
Cross-sectional Area cm^2	78.54	**EBCT min**	1.02
Biochar Bed Volume cm^3	3927	**M_{60} mg**	4350
Flow cm^3/min	4006	**Linear Velocity cm/min**	51

4.7 Analytical Method

The concentrations of phosphorus in the water samples prior to and after treatment were analysed with the HACH DR3900 Spectrophotometer at 880 nm. Its basic working principle is based on Beer's law, which states that the amount of light absorbed by a medium is proportional to the concentration of the substance in solution. Every chemical absorbs and transmits light over a certain range of wavelength. Generally, a spectrophotometer consists of two devices; a photometer and a spectrometer. A spectrometer emits a chosen range of wavelength of light and a photometer detects the amount of absorbed photons once the light has passed through a sample in an analytical cuvette (Atkins and De Paula, 2006). Beer-Lambert Law is written as:

$$A = \varepsilon lc$$

where A is the measure of absorbance, Ɛ is the molar absorptivity, l is the path length, and c is the concentration of the solute.

5 Results and Analyses

5.1 Bulk Density and Moisture Content

The results from the laboratory tests are summarized in the table below.

Table 6. Bulk density and moisture content of the biochar.

	Bulk Density (g/L)	**Moisture Content (%)**
1st test	226.95	9.21
2nd test	235.71	8.75
3rd test	220.69	11.62
4th test	223.77	12.93
5th test	228.31	11.24
Average	**227.09**	**10.75**
Standard Deviation	**5.65**	**1.74**

5.2 Batch Experiments

Results of the batch experiments are included in Table 7. The highest removal efficiency, 57.53%, was achieved at the following operating condition, pH = 7, initial TP concentration = 20, and biochar dosage = 2.5. As the TP concentration was raised to 40 mg/L, and the biochar dosage was reduced to 1.5 g, much lower removal efficiency, 15.25%, was detected. There was only a minor difference between the responses in two different trials, the 4th and 5th. This reflects the complexity and strong interaction between the variables.

Table 7. Experimental design matrix and removal efficiency.

Run Order	Coded Values			Physical Values			Removal Efficiency
	X_1	X_2	X_3	*pH*	*C*	*D*	
1	-1	-1	1	4	20	2.5	48.81
2	-1	-1	-1	4	20	1.5	42.79
3	-1	1	-1	4	40	1.5	53.35
4	1	-1	1	7	20	2.5	57.53
5	-1	1	1	4	40	2.5	56.95
6	1	-1	-1	7	20	1.5	39.14
7	1	1	1	7	40	2.5	31.76
8	1	1	-1	7	40	1.5	15.25
9	0	0	0	5,5	30	2	41.39
10	0	0	0	5,5	30	2	43.53
11	0	0	0	5,5	30	2	39.02
12	0	0	0	5,5	30	2	40.31

5.2.1 Regression Analysis

The main objective was to identify a function that explains the effect of individual variables and their interactions' on the TP adsorption efficiency of this biochar so that one can predict the change in the response when any change in the independent variables occurs. For this TP adsorption process, the coefficients β_0, β_2, and β_3 specify the effect of pH, initial TP concentration, and adsorbent dosage, respectively. Coefficients β_{12}, β_{13}, and β_{23} indicate the interacting effects of pH-initial concentration, pH-dosage, and initial concentration-dosage. Student's *t* test was applied to determine the significance

of the regression coefficients, and the *p*-values were used as means to check the level of significance. Generally, the smaller the value of *p*, the more significant is the coefficient term.

Analysis of variance (ANOVA) was performed to test the significance of the main effects and the two-way interactions within the model. The null hypothesis (H_0) for this test is that the main effects and the interactions are equal to zero, i.e. based on the available data, they do not have significant influence on the removal of TP. The alternative hypothesis (H_A) is that the main effects and the interactions are different from zero, i.e. they have significant influence on the response. Additionally, the ANOVA also provided the Fisher's variance ration and its corresponding *p*-value, which could be used to check the significance and adequacy of the model as a whole.

The two-way interaction between initial concentration and dosage, and the three-way interaction between all variables were determined to be insignificant (*p*-value > 0.05) (Table 8). On the contrary, the results showed that all main effects of the factors and interaction effects of X_1X_2 and X_1X_3 are highly significant (*p*-value < 0.05). Consequently, regression analysis was repeated with those insignificant interactions dropped from the model (Table 9). The *F*-statistic value for the model was high, 68.65, in comparison to the tabulated *F* value for α = 0.01 at 5 and 6 degrees of freedom (8.74), and the *p*-value was extremely small, 3.263e-05, which demonstrate the significance of this model.

The Pareto analysis is an informative graphical representation used to demonstrate the ranking of those variables and their interactions, on the basis of their cumulative effect on the response. A Pareto chart consists of a series of bars, whose heights reflect the impact of the parameters. Hence, the ones represented by taller bars are more significant. The effect of each parameter was calculated according to Eq. (11).

$$P_i = \left(\frac{b_i^2}{\sum b_i^2}\right) \times 100 \quad (i \neq 0) \qquad \text{(Eq. 11)}$$

As demonstrated in Figure 1, the results of the ANOVA can be conveniently portrayed in a bar chart. The R codes used to make the plot are included in Appendix 1.

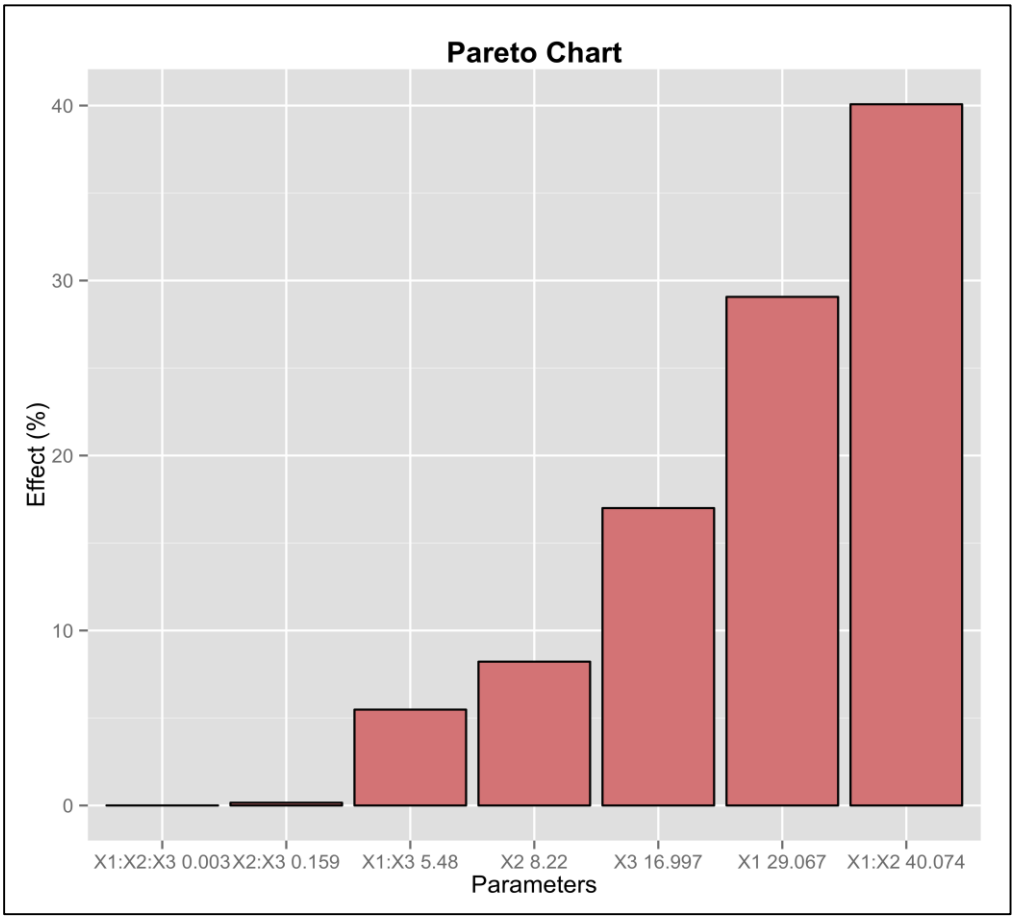

Figure 1. Pareto chart shows the ranking of the proportional effects of the parameters on the removal efficiency.

Table 8 and table 9 contain the summary outputs of the statistical results.

Table 8. Results of the first regression analysis for TP adsorption removal efficiency.

	Coefficient	**Std. Error**	**t-value**	**p-value**	**Significance Code**
Intercept	42.48	0.6936	61.26	4.25e-07	***
X_1	-7.28	0.8494	-8.56	0.001	**
X_2	-3.87	0.8494	-4.55	0.010	*
X_3	5.56	0.8494	6.55	0.002	**
X_1X_2	-8.54	0.8494	-10.06	0.000	***
X_1X_3	3.16	0.8494	3.72	0.020	*
X_2X_3	-0.53	0.8494	-0.63	0.561	Not significant
$X_1X_2X_3$	0.06	0.8494	0.08	0.940	Not significant
R^2	98%	***F*-statistic**	36.07	**Res. error**	2.403
Adj. R^2	95%	***p*-value**	0.0018		

Table 9. Results of the second regression analysis, in which insignificant terms had been dropped.

	Coefficient	Std. Error	t-value	p-value	Significance Code
Intercept	42.49	0.5944	71.48	5.05e-10	***
X_1	-7.28	0.7280	-9.99	5.80e-05	***
X_2	-3.87	0.7280	-5.31	0.001	**
X_3	5.56	0.7280	7.64	0.000	***
X_1X_2	-8.54	0.7280	-11.73	2.31e-05	***
X_1X_3	3.16	0.7280	4.34	0.004	**
R^2	98%	***F*-statistic**	68.65	**Res. error**	2.403
Adj. R^2	96%	***p*-value**	3.263e-05	**LOF's p**	0.41

The regression equation in coded units (Eq. 12) was established from the batch experiments by substituting the coefficients of significant terms into Eq. (8). The sign (-) of pH-initial concentration interaction (X_1X_2) implied its negative impact on the response. It also had the highest effect, according to the magnitude shown in Figure 1. Conversely, the interaction between pH and biochar dosage (X_2X_3) resulted in an increase in adsorptive capacity, as indicated by the (+) sign.

$$Y = 42.49 - 7.28X_1 - 3.87X_2 - 3.31X_3 - 8.54X_1X_2 + 5.41X_1X_3 \quad \text{(Eq. 12)}$$

5.2.2 Lack-of-fit Test

Since 4 replicates of the centre point had been added to the experimentation, a lack-of-fit test could be performed to evaluate the reliability of the model in explaining the obtained data. The null hypothesis of this test (H_0) states that there is no lack of fit in the model, and the alternative hypothesis (H_A) is that there is a lack of fit in the model. In case a lack-of-fit is present, it indicates that the data is more complex, so the model cannot describe appropriately. The value for lack-of-fit *F*-statistic was 1.32 at 3 degrees of freedom and the corresponding *p-value* is 0.41. For the reason that *p-value* is larger than the significance level α = 0.05, the null hypothesis was not rejected, i.e. the evidence indicates that there is no lack of fit.

5.2.3 Non-linearity Test

In addition, it was possible to implement a non-linearity test to check for the significance of curvature. The null hypothesis (H_0) of this test is that the effect of curvature is not significant, and the corresponding alternative (H_A) is the effect of curvature is significant. The *p-value* suggested keeping the hypothesis (*p-value* = 0.585 > 0.05), specifying that the linear model is suitable.

5.2.4 Adjusted Determination of Coefficient

The model presented an adjusted square correlation coefficient R^2 of 95.71%, which is the proportion of the variation of the response explained by this model, taking into account the degrees of freedom. Generally, it is a more realistic estimation of goodness of fit (Box et al., 2005). Another test showed the Q^2 to be 93.33%, which is fairly comparable to the adjusted R^2. This is another evidence indicating the adequacy of this model.

5.2.5 Two-way Interaction Effects

As pair-wise interactions between pH-concentration and pH-dosage were found to be significant, the main effect of individual variable was not interpreted. Instead, the interacting factors were examined jointly. Any attempt to interpret main effects in the presence of significant interactions might lead to confusion and false conclusions. Interaction plots are useful means to illustrate the relationship between two variables graphically. In order to analyse obtained information, an interaction plot was created for each pair, which contains the mean response of two factors at all possible combinations of their level settings. If the lines are non-parallel, it indicates the presence of interaction between the factors. On the other hand, there is no interaction between a pair of factors if the lines are parallel.

Figure 2 displays a strong interaction between pH and initial concentration of TP (Initial C) because two lines intersected. The effect of pH at different levels of initial TP concentration was noticeably different. A significant decrease of TP removal efficiency was observed when the pH level increased from 4 to 7 at higher initial TP concentration. However, it was the opposite in the case of lower initial TP concentration. By increasing

the pH, a slight increase of TP uptake occurred. Additionally, at higher TP concentration, the response was much more sensitive to pH variation, as indicated by high magnitude of TP removal in the plot. Conclusively, the highest TP removal efficiency was achieved when pH was set at low level, 4, and the initial concentration was at high level, 40 mg/L. This could be due to stronger driving force by a higher concentration gradient pressure, which ultimately led to more effective utilization of the adsorptive capacities of the biochar (Bhargava and Sheldarkar, 1993).

As presented in Figure 3, there exists an interaction between pH and biochar dose, though not as substantial as the one between pH and TP concentration. In both circumstances, increasing the pH led to a decrease in the response. At lower biochar dosage, the response was more sensitive to changes in the pH. It was clear that low pH was more beneficial at all studied levels of biochar dose. Maximum TP uptake was observed at the following operating condition, pH = 4, and biochar dosage = 2.5 g.

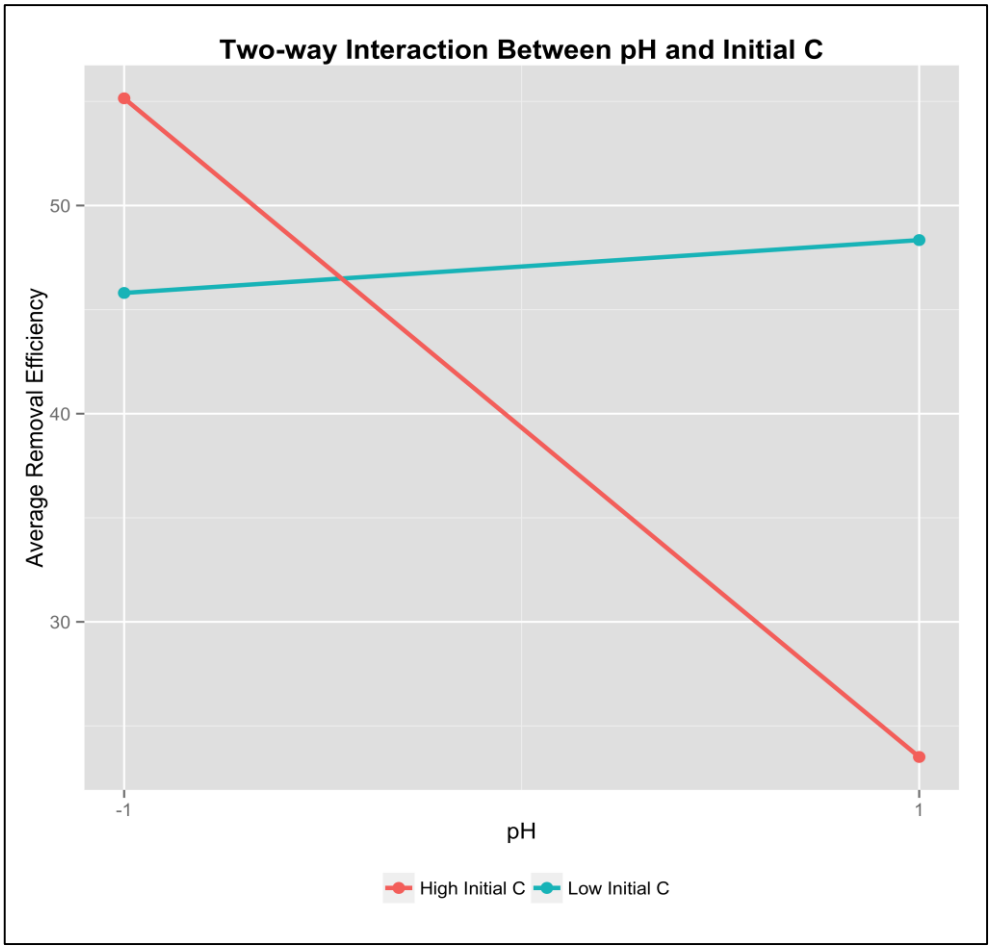

Figure 2. Two-way interaction between pH and initial TP concentration.

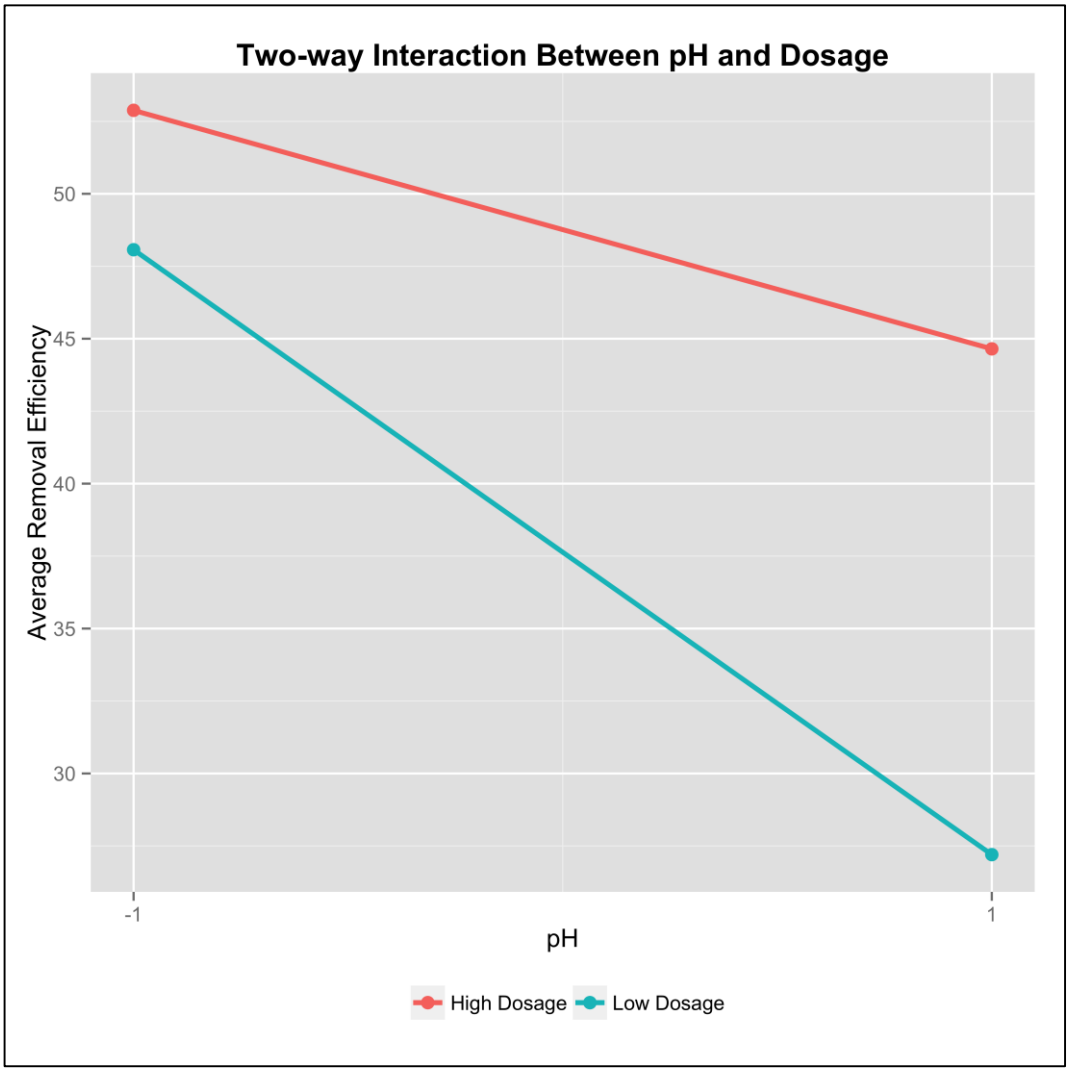

Figure 3. Two-way interaction between pH and biochar dose.

5.3 Fixed-bed Column

As can be seen in Figure 4, the removal efficiency of the system decreased over time as bed volumes increased in both tests. Due to the limited number of available cuvettes, only 4 samples were collected and analysed after 1 hour for each experiment. However, the curves are expected to reach their peaks (i.e. saturation point), then level off, forming an S-curve shape. The breakthrough occurred faster with a higher flow rate (4.01 L/min). Assuming that the breakthrough point was when the TP concentration in the effluent equals to 90% of the influent concentration, the saturation time was reached faster at a higher flow rate after 1 hour. The contact time between the particles and the solution was longer (higher EBCT, as calculated in Table. 4, page 24), which led to higher removal of TP. At flow rate of 4.7 L/min, the adsorption capacity was lower

because of insufficient residence time and low diffusion of the solute into the pores of biochar in the column. Furthermore, at higher flow rate, the rate of mass transfer increases (higher M_{60}, as calculated in Table. 5, page 24), resulting in more TP being sent through the adsorbent bed during the same amount of time. Ultimately, this reduces the removal efficiency of the system and leads to faster saturation time. The rate of efficiency degradation occurred much faster when the process was being operated at V = 4.12 L/min, as demonstrated by a steeper slope between *t* = 15 and *t* = 30.

In both cases, the effluent pH increased considerably from 5.5 to over 6 after 15 min of operation and then the rate slowed down. This might be due to the alkalinity of biochar, which also makes it a natural soil amendment to neutralize soil acidity (Chan et al., 2007; Yuan et al., 2011). At a lower flow rate, there was a faster increase of pH because the residence time was longer than that at high flow rate.

Overall, the TP adsorptive capacities of the unmodified biochar were low in comparison to other natural adsorbents. It only took some bed volumes to degrade the uptake efficiency. In practice, this means that the biochar bed is subjected to backwashing or replacement after short time-length. The following tables contain operating parameters at different flow rates. The removal efficiency was calculated according to Eq. (6).

Table 10. Parameters of the effluent at flow rate = 2.67 L/min.

Time (min)	Effluent C (mg/L)	C_t/C_i	Removal Efficiency (%)	Effluent pH
15	8.7	0.48	42.50	6.47
30	9.5	0.52	30.44	6.53
45	9.7	0.54	24.22	6.68
60	10.7	0.59	16.50	6.77

Table 11. Parameters of the effluent at flow rate = 4.01 L/min.

Time (min)	Effluent C (mg/L)	C_t/C_i	Removal Efficiency (%)	Effluent pH
15	13.05	0.73	27.5	6.02
30	14.98	0.83	16.8	6.13
45	15.71	0.87	12.7	6.19
60	16.38	0.91	9.0	6.26

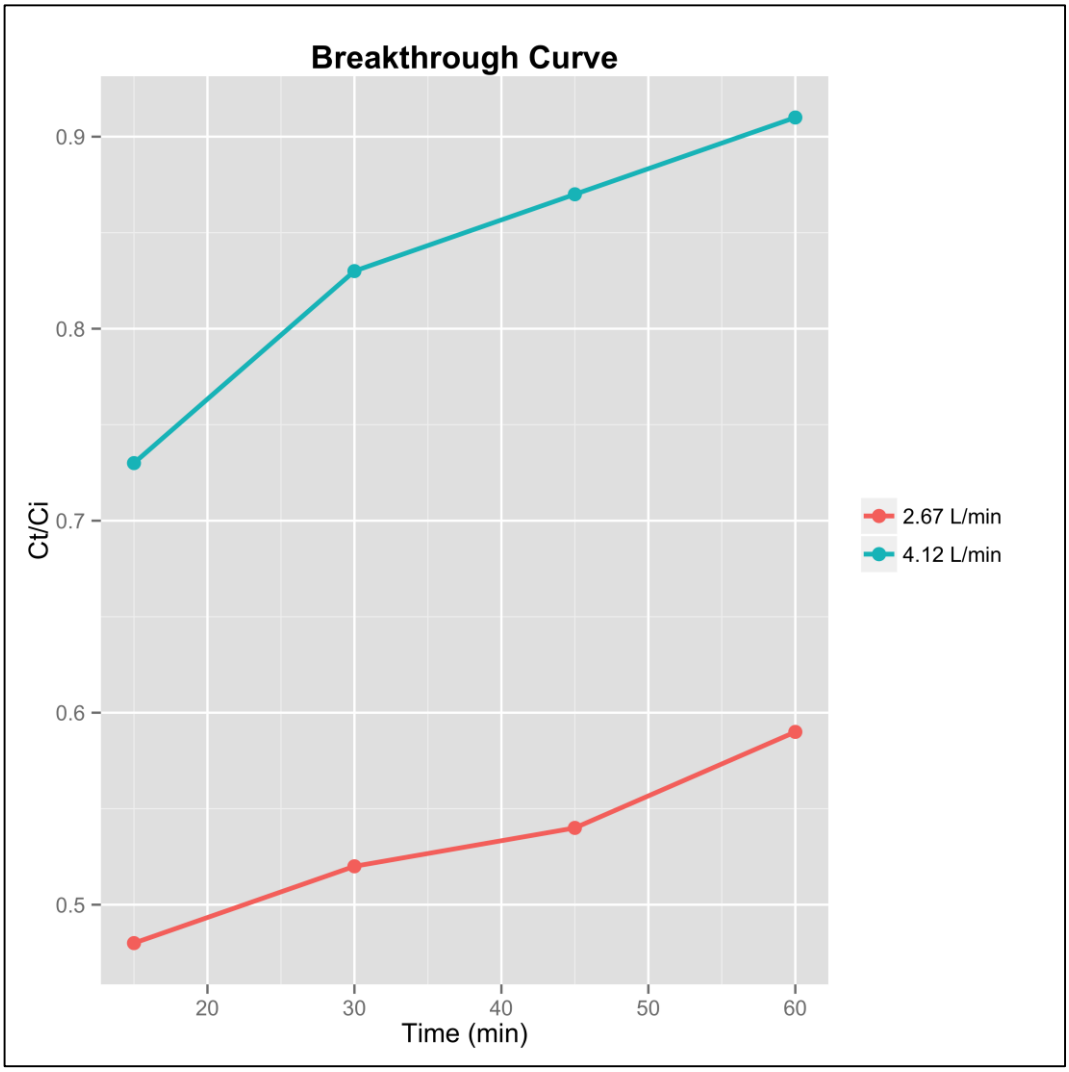

Figure 4. Breakthrough curve at different flow rates.

6 Discussion & Conclusions

6.1 Discussion

The first objective of this thesis was to study the effects of different regulating parameters on total phosphorus removal efficiency by biochar enhanced with Fe^{3+}. It was found that the highest removal efficiency (57.53%) in the studied region occurred at the following condition, pH = 7, TP concentration = 20 mg/L, and biochar dosage = 2.5 g. However, a relatively similar removal (56.95%) was seen when the pH was lower (4) and the initial concentration was higher (40 mg/L).

Generally, low pH and high adsorbent dosage resulted in much better adsorption efficiency. Additionally, one interesting result was that at high initial concentration, 40 mg/L in this case, the response was momentously sensitive to variation in pH, i.e. lower pH led to much higher removal efficiency. Better performance was seen at high concentration level. This could be attributed to higher concentration gradient pressure at higher concentration level, which created stronger driving force. The outcome was better utilization of adsorptive sites. This discovery has been reported in the literature.

In case the initial concentration was half the highest amount, 20 mg/L, pH alteration did not affect considerably, and the efficiency was actually higher at higher pH, though not substantial. At low biochar dosage level, pH adjustment seriously impeded the uptake efficiency, resulting in a drop of about 21%. This observation showed that adding more adsorbent makes the negative impact of high pH less influential.

The second goal of this study was to investigate the effect of flow rate on TP adsorption efficiency in a fixed-bed column apparatus. For these experiments, natural biochar was used to assess its real adsorption ability. Bed height, initial pH level, and influent temperature were the same for both tests. It was observed that greater removal of TP from wastewater was achieved at lower flow rate. Moreover, the saturation point, at which the final concentration in the effluent is similar to that of the influent, occurred much faster when the operating flow rate was higher. Longer contact time (EBCT) between the solution and the adsorbent led to higher removal efficiency. The results also showed that by increasing the flow rate, the speed of exhaustion also increased, leading to a decrease in the service time of the bed. As the flow rate increased, the contact time declined, which resulted in a lower diffusivity of the solute among the particles of the biochar.

6.2 Conclusions

Overall, although the natural biochar possesses some adsorption capacity to remove phosphorus from wastewater, its adsorption efficiency was not as high as expected. In the case of packed-column process, the 50-cm natural biochar bed only removed approximately 40% of incoming phosphorus at its maximum capacity and the efficiency started to decrease after only 15 min of operation. By that time, merely 60 L of wastewater had passed through the bed. At 4 L/min, the saturation point was reached after 1 hour of operation and about 61 bed volumes had been passed through the col-

umn by that time. However, depending on intended use and water standards, its effectiveness can be graded differently. Furthermore, it can be applied jointly with other low-cost natural adsorbents or inexpensive technologies to treat wastewater more efficiently. In batch experiments, the biochar enhanced with Fe^{3+} adsorbed from 45% to 55% of phosphorus. All the independent variables, pH, biochar dosage, and initial phosphorus concentration were found to be important in affecting the removal efficiency. Additionally, further analysis showed that there were strong interactions in these pairs: pH-concentration and pH-dosage. The ranking of significant effects was in the order of *pH:Initial concentration* > *pH* > *Dosage* > *Initial concentration* > *pH:Dosage*. An empirical model was developed to predict the response as a function of relationships among chosen variables.

$$Y = 42.49 - 7.28X_1 - 3.87X_2 - 3.31X_3 - 8.54X_1X_2 + 5.41X_1X_3$$

6.3 Limitations and Suggestions

The total composition of the wastewater was not fully known. Thus, presence of some chemicals might have affected the results. The equilibrium time for the batch experiments was presumed to be 1 hour. Even though the assumption was based on the literature, the necessary contact time might be longer than that. Hence, a study on effect of contact time with different concentrations might be valuable. Samples should be taken at regular intervals for some hours, preferably. Then it can be checked to see if the process follows first-order kinetics or second-order kinetics. Since the biochar was manually crushed for the column tests, differences in size and shape distributions might have negative effect on the efficiency. In addition, one could perform Central Composite Design method, in which axial points are added to the design matrix, which helps find the optimum operating conditions to achieve the highest removal efficiency.

Another promising approach would be to produce biochar from known and carefully selected materials under favourable temperatures and heating rates. Different biochar types made of different precursors can then be used to test the difference in their TP uptake capacities. In addition to that, biochar can also be examined for its ability to adsorb heavy metals.

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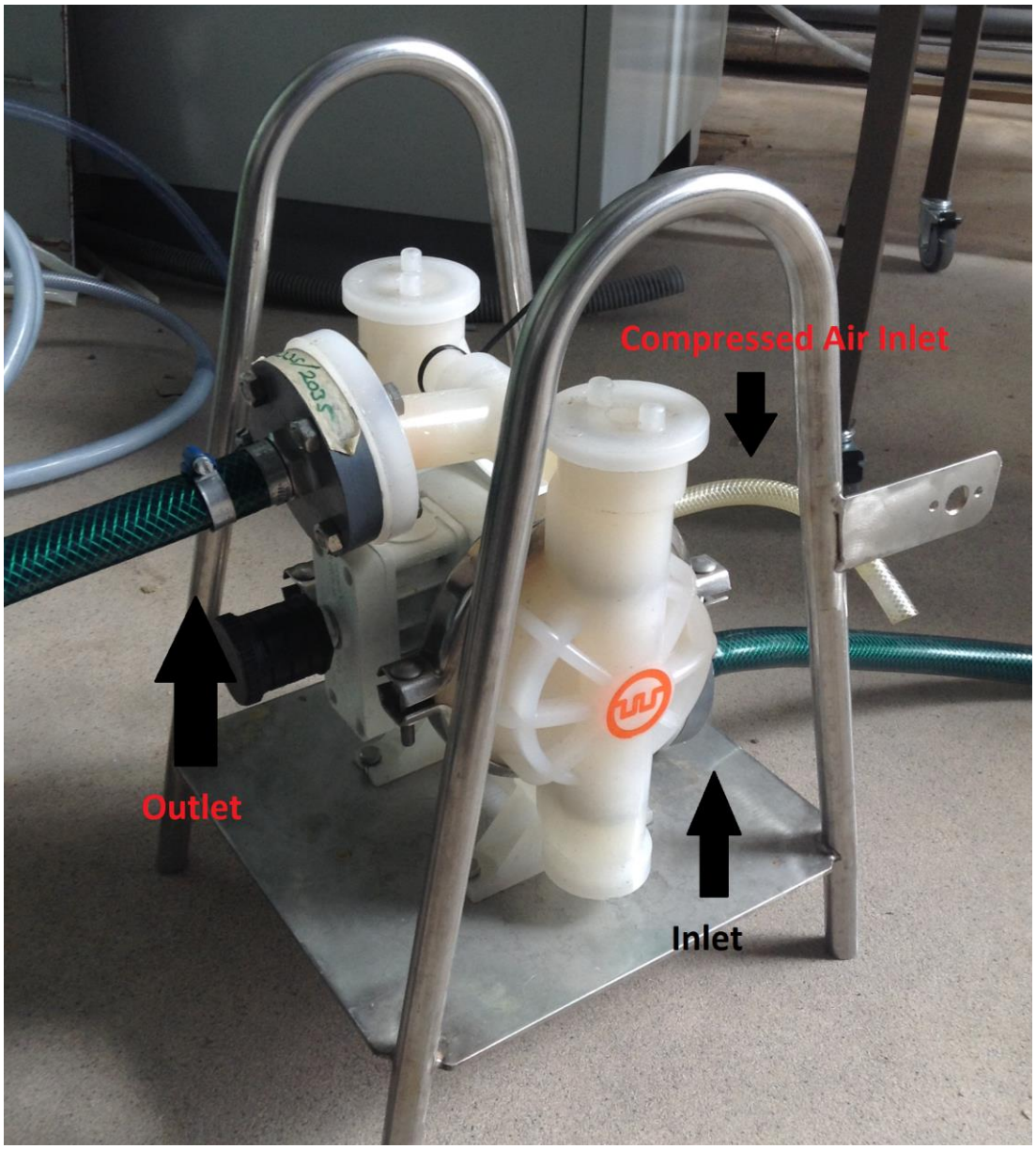
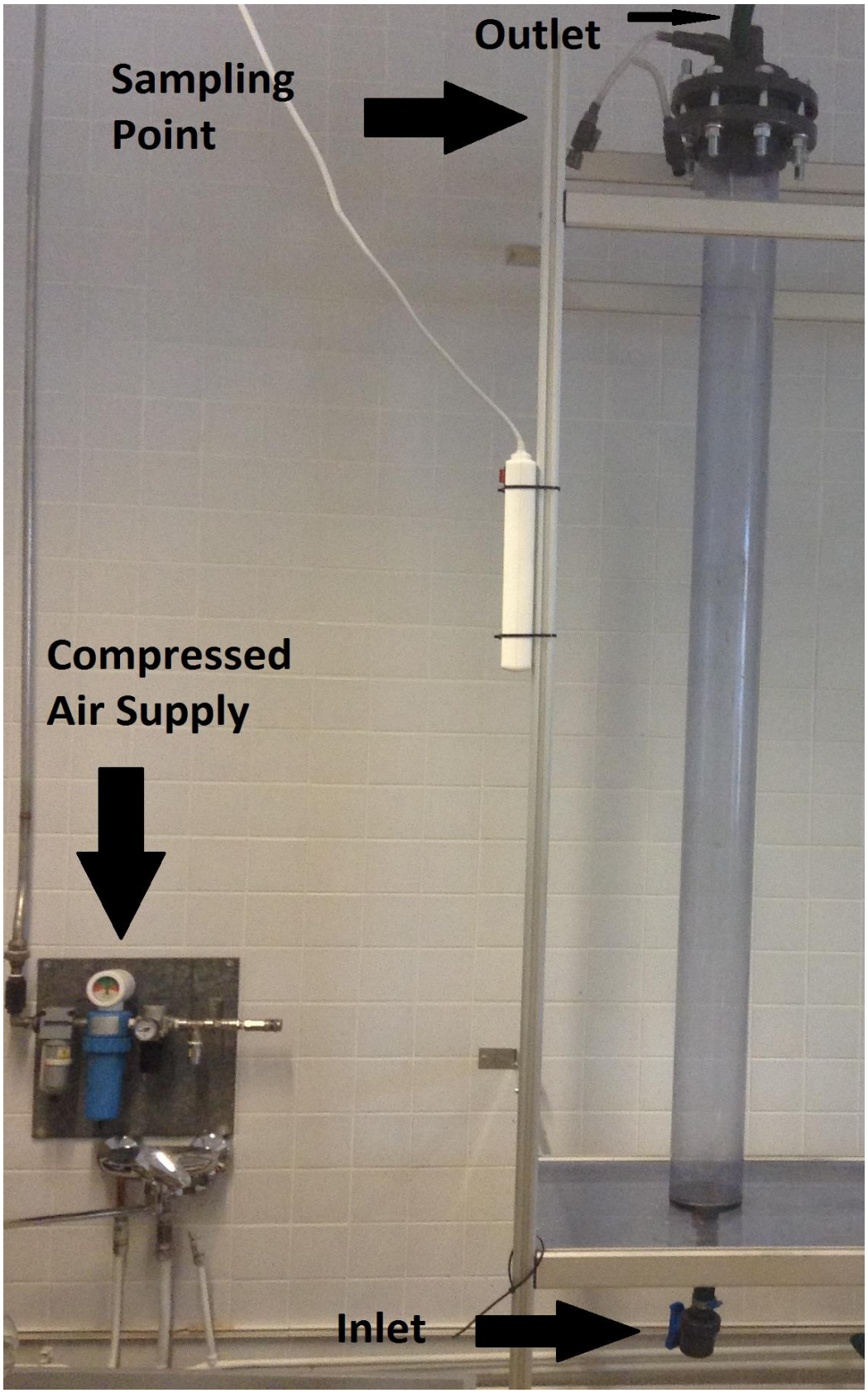
Wastewater Composition

Parameter	COD mg/l	BOD7 mg/l	Total N mg/l	TDS mg/l
Value	19000	13000	490	4

Diaphragm Pump



Fixed-bed Column Apparatus



Codes to create the plots

```
library(ggplot2)

cbbPalette = c("#000000", "#E69F00", "#56B4E9", "#009E73", "#F0E442", "#0072B2", "#D55E00", "#CC79A7")

# Plot of the Breakthrough Curve

df = data.frame(x=seq(15,60,15),y1=c(.48,.52,.54,.59),y2=c(.73,.83,.87,.91))
cls1 = c("2.67 L/min"="#0072B2","4.12 L/min"="#D55E00")

g = ggplot(df, aes(x), xlim=c(15,60)) + ggtitle("Breakthrough Curve") + theme(plot.title = element_text(lineheight=1.5, face="bold"),legend.title=element_blank())
g = g + geom_line(aes(y=y1,group="2.67 L/min", colour="2.67 L/min"),size=1.0) + geom_line(aes(y=y2,group="2.67 L/min",colour="4.12 L/min"),size=1.0)
g = g + geom_point(aes(y=y1, colour="2.67 L/min", fill="2.67 L/min"),size=3) + geom_point(aes(y=y2,colour="4.12 L/min", fill="4.12 L/min"),size=3)
g = g + labs(x = "Time (min)", y = "Ct/Ci")
ggsave("l3374.png",dpi=600)

# Plot of the Pareto Chart

df1 = data.frame(x=c("X1:X2","X1","X3","X2","X1:X3","X2:X3","X1:X2:X3"),y=c(40.074,29.067,16.997,8.220,5.480,0.159,0.003))
df1 = transform(df1, category=factor(paste(x,y)))
df1 = transform(df1, category=reorder(category, rank(y)))

pc = ggplot(df1, aes(category,y)) + geom_bar(stat = "identity", colour="black", fill="#DD8888") + labs(x = "Parameters", y = "Effect (%)")
pc = pc + ggtitle("Pareto Chart") + theme(plot.title = element_text(lineheight=1.5, face="bold"))
ggsave("leu1.png",dpi=600)

# Plot of the two-way interaction pH:C

df2 = data.frame(x=c(-1,1),y1=c(45.8,48.34),y2=c(55.15,23.51))
cls2 = c("Low Initial C"="#0072B2","High Initial C"="#D55E00")

ip = ggplot(df2, aes(x)) + geom_line(aes(y=y1, colour="Low Initial C"), size=1.1,) + geom_line(aes(y=y2,colour="High Initial C"),size=1.1)
ip = ip + geom_point(aes(y=y1,colour="Low Initial C", fill="Low Initial C"),size=3) + geom_point(aes(y=y2, colour="High Initial C", fill="High Initial C"),size=3)
ip = ip + theme(plot.title = element_text(lineheight=1.5, face="bold"),legend.title=element_blank(), legend.position="bottom")
ip = ip + labs(x = "pH", y = "Average Removal Efficiency") + scale_x_continuous(breaks=c(-1,1))
ip = ip + ggtitle("Two-way Interaction Between pH and Initial C")
ggsave("buk1.png",dpi=600)

# Plot of the two-way interaction pH:D

df3 = data.frame(x=c(-1,1),y1=c(48.07,27.20),y2=c(52.88,44.65))
cls3 = c("Low Dosage"="#009E73","High Dosage"="#D55E00")

ip2 = ggplot(df3, aes(x)) + geom_line(aes(y=y1, colour="Low Dosage"), size=1.1,) + geom_line(aes(y=y2,colour="High Dosage"),size=1.1)
ip2 = ip2 + geom_point(aes(y=y1,colour="Low Dosage", fill="Low Dosage"),size=3) + geom_point(aes(y=y2, colour="High Dosage", fill="High Dosage"),size=3)
ip2 = ip2 + theme(plot.title = element_text(lineheight=1.5, face="bold"),legend.title=element_blank(), legend.position="bottom")
ip2 = ip2 + labs(x = "pH", y = "Average Removal Efficiency") + scale_x_continuous(breaks=c(-1,1)) + scale_y_continuous(breaks=seq(15,60,5))
ip2 = ip2 + ggtitle("Two-way Interaction Between pH and Dosage")
ggsave("buk2.png",dpi=600)
```

Codes to create the design matrix and analyze the results

```r
source('http://users.metropolia.fi/~velimt/Environmetrics/II/DOE_functions_v4.2d.r') # R package scripted by Veli-Matti Taavitsainen for DOE
minx <- c(4,20,1.5)
maxx <- c(7,40,2.5)

X = mton(2, 3, 4)          # Generates a 2^3 factorial design with 4 center points
Xdec = decode(X,minx,maxx) # Decode coded units to physical values
Xran = randomize(Xdec)     # Randomization before conducting the experiments

data <- read.table('results.txt',header=TRUE)  # Read in the results
x <- data[,1:3]
y <- data[,4]

X1 = data$pH
X2 = data$C
X3 = data$D

# 1st model with all terms

model1 = quad.model.fit(x,y,1.5)
print(summary(model1))

# 2nd model with only significant terms

model2 = quad.model.fit(x,y,1.5,terms=c(1:5))
print(summary(model2))

# Non-linearity test

model2$nonlin.test

# Lack-of-fit test

print(model2$LOF)

# Q-squared test

print(model2$Q)

# Tabulated F-value

qf(.99,df1=5,df2=6)
```

Outputs of Regression Analysis + ANOVA

Model 1

```
Coefficients:
            Estimate Std. Error t value Pr(>|t|)
(Intercept)  42.4858     0.6936  61.258 4.25e-07 ***
pH           -7.2775     0.8494  -8.567 0.001019 **
C            -3.8700     0.8494  -4.556 0.010370 *
D             5.5650     0.8494   6.551 0.002807 **
pH:C         -8.5450     0.8494 -10.060 0.000549 ***
pH:D          3.1600     0.8494   3.720 0.020472 *
C:D          -0.5375     0.8494  -0.633 0.561249
pH:C:D        0.0675     0.8494   0.079 0.940480
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 2.403 on 4 degrees of freedom
Multiple R-squared:  0.9844,   Adjusted R-squared:  0.9571
F-statistic: 36.07 on 7 and 4 DF,  p-value: 0.001865
```

Model 2

```
Coefficients:
            Estimate Std. Error t value Pr(>|t|)
(Intercept)  42.4858     0.5944  71.479 5.05e-10 ***
pH           -7.2775     0.7280  -9.997 5.80e-05 ***
C            -3.8700     0.7280  -5.316 0.001802 **
D             5.5650     0.7280   7.645 0.000262 ***
I(pH * C)    -8.5450     0.7280 -11.738 2.31e-05 ***
I(pH * D)     3.1600     0.7280   4.341 0.004871 **
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 2.059 on 6 degrees of freedom
Multiple R-squared:  0.9828,   Adjusted R-squared:  0.9685
F-statistic: 68.65 on 5 and 6 DF,  p-value: 3.263e-05
```

```
> model2$nonlin.test
difference          t          p
2.13500000 2.98222349 0.05849292
> model2$LOF
         FLOF          pLOF sd.pure.error df.pure.error
    1.3264251     0.4109686     1.9090901     3.0000000
> model2$Q
[1] 0.9338956
> qf(.99,df1=5,df2=6)
[1] 8.745895
```